This thesis has been divided into six chapters:

Chapter 1: Introduction

This chapter provides a brief introduction related to the background and structure of the perovskite oxides and ferrites. In addition to this, literature survey describing current status as well as structural, transport and magnetic properties of these materials has been discussed. It starts with an introduction of mixed metal oxides followed by various physical properties of these oxides.

Chapter 2: Synthetic and characterization techniques

In this chapter, the techniques of synthesis of solid-state materials and characterization techniques used during the research have been discussed. The preparatory methods like pechini method and combustion method has been discussed briefly in this chapter. Various different methods used for characterization of mixed metal oxides like Powder X-ray Diffraction (XRD), Rietveld refinements, Scanning Electron Microscopy (SEM), Energy Dispersive X-ray spectroscopy (EDX), Transmission Electron Microscopy (TEM), Thermogravimetric and Differential thermal analysis (TG-DTA), Vibrating sample magnetometer (VSM), Faraday magnetic measurement system, and standard four-probe resistivity measurement system have been explained.

Chapter 3: Enhanced coercivity of NiFe$_{1-x}$Dy$_x$CrO$_4$ ferrites synthesized by glycine-nitrate combustion method

This chapter describes the experimental results of Dy incorporated nickel ferrite NiFe$_{1-x}$Dy$_x$CrO$_4$ prepared by a glycine-nitrate combustion process. The structural characterization and phase purity of the samples was done using using X-ray powder diffraction using CuK$_\alpha$ radiation ($\lambda = 1.5406$ Å). The refinement of the samples was started with scale and background parameters followed by the unit cell parameters. The XRD data was fitted using the Rietveld’s refinement software, the GSAS/EXPGUI program which indicates that all the ferrites crystallize in cubic symmetry corresponding to the space group $Fd\overline{3}m$ with small amounts of secondary phase DyFeO$_3$. With
increasing Dy content, the characteristic peak of DyFeO$_3$ gradually increases. This implies that Dy$^{3+}$ has limited solid solubility. The thermal study of the precursor gels was done by using Thermogravimetric and Differential thermal analysis (TG-DTA). The thermo-analytical pattern manifests that the two discrete weight loss steps of precursors is observed with increasing temperature from ambient till 1000°C. Initially a small mass loss of 10% was observed at 190 °C that can be attributed to the volatilization of water of crystallization and evaporation of remaining ethylene glycol, associated with endothermic DTA peak. A second large weight loss is observed in the temperature range of 190–200°C due to occurrence of combustion reaction due to the interaction of glycine and nitrate ions in the gel with the liberation of water, CO$_2$ and N$_2$ and formation of ferrite which is associated with an exothermic peak around 200°C in the DTA curve. The chemical composition for the constituent elements of the synthesized bulk samples has been analyzed by using Energy dispersive X-ray (EDX) using INCA attachment with the SEM instrument. The results confirmed the existence of the constitutive elements Ni, Fe, Cr, Dy and O. The EDX results did not show any impurity element in the phases, and the compositions are in agreement with the compositions calculated from the formula. The microstructures and grain sizes of the calcined ferrite samples were estimated by SEM technique considering the average of large number of grains. Room temperature magnetization results, obtained from VSM measurements, showed a decrease in saturation magnetization with Dy doping. Enhanced coercivity in undoped Ni-Cr ferrite is observed whose magnitude was much higher than that of the reported bulk material. Substitution of Dy in Ni-Cr ferrite further enhances coercivity thereby making the materials magnetically more hard.

**Chapter 4: Influence of alkali substitution in La$_{0.7}$Ca$_{0.3}$Mn$_{0.8}$Cr$_{0.2}$O$_3$ perovskite manganites on structural, magnetic and transport properties**

In this chapter, the study of the effect of A-site cation mismatch on the structural, magnetic and transport properties, a systematic investigation of La$_{0.7}$Ca$_{0.25}$A$_{0.05}$Mn$_{0.8}$Cr$_{0.2}$O$_3$ (A = Ca, Li, Na, K) has been undertaken. These samples were synthesised by combustion method using glycine as a fuel. The materials used in the synthesis were La(NO$_3$)$_3$.6H$_2$O, CaCO$_3$, Li$_2$CO$_3$, Na$_2$CO$_3$, K$_2$CO$_3$, Mn(CH$_3$COO)$_2$, Cr(NO$_3$)$_3$.9H$_2$O and
glycine. Detailed structural analysis of the oxides has been carried out using powder X-ray diffraction (PXRD) Rigaku SmartLab 9kW rotating anode with CuKα radiation in the 2θ range 10–100°. The orthorhombic symmetry of samples corresponding to the Pbnm space group is confirmed by Rietveld refinements. The chemical composition for the constituent elements of the synthesized samples has been analysed by using Energy dispersive X-ray (EDX). The results confirmed the existence of the constitutive elements and did not show any impurity element in the phases. All compositions except one containing K are in agreement with the compositions calculated from the formula. The results show that some K is vaporized during sintering. The results of iodometric titrations suggest that all the phases were oxygen stoichiometric except one containing K which was oxygen deficient. Oxygen deficiency in K sample is due to vaporization of K as confirmed from EDX. Scanning electron microscopy was done to know the topography of the synthesized alkali substituted manganites. It is apparent from the micrographs that the materials are fine-grained and the particle sizes are uniformly distributed. These graphs shows that grain size increases slightly with the addition of alkali metal from Li to K due to increase in size of the doping element. Magnetic susceptibility as a function of temperature in liquid nitrogen from 80 to 300 K was measured by Faraday magnetic balance using mercury(II)tetrathiocyanatocobaltate(II) as a calibrant. A paramagnetic to ferromagnetic transition at low temperature is observed in all the samples. The ferromagnetic behaviour of the phases is due to the fact that all the phases contain Mn in mixed valence state of +3 and +4. This results in formation of Mn$^{3+}$/Mn$^{4+}$ pairs which leads to double exchange interaction. The $T_C$ value was found to increase with increasing $<r_A>$. The reason is that the increase of $<r_A>$ straightens the Mn–O–Mn angle in perovskites, thereby enhances the band width. This decreases the tendency of hopping of $e_g$ electron from Mn$^{3+}$ to Mn$^{4+}$ and therefore an increase $T_c$ is observed. We have measured the magnetization as a function of applied magnetic field $M$–$H$ for La$_{0.7}$Ca$_{0.25}$A$_{0.05}$Mn$_{0.8}$Cr$_{0.2}$O$_3$ at 10K with the sweep field 7T. With application of a small field, the magnetization $M$ increases rapidly and then inclines to saturation, which exhibits a spontaneous magnetizing process of the FM phase. The electrical Resistivity was measured as a function of temperature by standard four-probe technique in the liquid nitrogen temperature range. Resistivity measurement displays a continuous increase in
resistivity with decreasing size, indicating semiconducting behaviour of samples. It can be seen that resistivity first increases with Li doping, then decreases with Na and finally increases with K doping. The variation of resistivity with alkali ion substitution could be explained on the basis of A-site cation radius $<r_A>$. The increase in $<r_A>$ increases the Mn–O–Mn angle which enhances the band width thereby decreasing resistivity. However, increase of resistivity of K sample with $<r_A>$ could be due to the oxygen deficiency. It has been concluded the conduction mechanism was dominated by Small polaron hopping model in the high temperature paramagnetic semiconducting region and the transport properties are dominated by SPH model.

Chapter 5: Effect of A-site disorder of heavier rare earth ion on structural, magnetic and transport properties of lanthanum based chromium manganite perovskite system

In order to study the effect of A-site cation mismatch on the structural, magnetic and transport properties, a systematic investigation of La$_{0.6}$Rh$_{0.1}$Ca$_{0.3}$Mn$_{0.9}$Cr$_{0.1}$O$_3$ (A = La, Eu and Ho) has been undertaken. We have discussed the effect of size of doped rare earth ion on the crystal structure, electrical and magnetic properties of the system. Phase identification was conducted using an X-ray powder Rigaku SmartLab 9kW rotating anode with Ni-filtered CuKα radiations at room temperature by collecting the data in a 2θ range of 10°–100°. The XRD data were analyzed by Rietveld refinements using the GSAS software. The sharp and intense peaks corresponding to the perovskite manganite phases were observed, signifying good crystalline forms for samples. All the analysed peaks for each sample can be well indexed to an orthorhombic crystal structure (space group Pbnm) without any impurities within the measurement range studied. The chemical composition for the constituent elements of the synthesized samples has been analysed by Energy dispersive X-ray spectroscopy (EDX). The results confirmed the existence of the constitutive elements and did not show any impurity element in the phases. The results of iodometric titrations suggest that all the phases were oxygen stoichiometric. The results further suggest that Mn in all the phases is present in mixed valence state of +3 and +4. Scanning electron microscope technique was performed to explore the morphology of the samples. The huge random agglomerated and aggregated grains of few micrometer length
scales are observed. Also, the clustering of the particles into the mini- or macro-aggregates with random shapes and sizes is evident. The SEM analysis also indicates that substitution of La by Eu and Ho has minor effect on grain shape and size. Magnetic susceptibility as a function of temperature in liquid nitrogen from 80 to 300 K was measured by Faraday magnetic balance using mercury(II)tetrathiocyanatocobaltate(II) as a calibrant. The magnetic properties of La$_{0.6}$R$_{0.1}$Ca$_{0.3}$Mn$_{0.9}$Cr$_{0.1}$O$_3$ (R = La, Eu and Ho) has been studied with a fixed concentration of the rare-earth ion, to probe the roles of Eu$^{3+}$ and Ho$^{3+}$ ions in determining magnetic behaviour. It has been observed that the value of $T_c$ decreases with decreasing $<r_A>$. The decrease in $T_c$ and magnetization values with the substitution of La$^{3+}$ by smaller rare-earth ions Eu and Ho can be interpreted in terms of Mn/Cr–O–Mn/Cr bond angle which signifies the extent of Mn ($e_g$) and O (2$p$) orbital overlap and hence plays a significant role in determining the electronic bandwidth and the magnetic exchange interaction. It is well known that size mismatch effect occurs when the doped rare earth ions are smaller than La to fill the space in the octahedral MnO$_6$ and, consequently, results in a more distorted structure and Mn/Cr–O–Mn/Cr bond bending. In the high temperature region, $\rho$–$T$ plot displays a continuous increase in resistivity with decreasing temperature, indicating semiconducting behavior of samples. It can be seen that resistivity increases with the substitution of heavier rare earth ion while there is reduction in $T_{MS}$. This variation could be explained on the basis of A-site cation radius $<r_A>$. The electronic conduction in these materials is obtained via hopping of electrons from the occupied sites, Mn$^{3+}$ ions, to the unoccupied sites Mn$^{4+}$/Cr$^{3+}$ ions (holes). The decrease in $<r_A>$ decreases the Mn/Cr–O–Mn/Cr angle. This may result a decrease in the tendency of hopping of $e_g$ electrons from Mn$^{3+}$ to Mn$^{4+}$/Cr$^{3+}$ sites thereby causing an increase in resistivity and reduction in $T_{MS}$. The transport properties are dominated by SPH model with polaron hopping energy increases with decreasing $<r_A>$.  

Chapter 6: Comparative study of La$_{0.5}$Nd$_{0.2}$Ca$_{0.3}$–$x$K$_x$MnO$_3$ ($x = 0.0$ and 0.05) nanoparticles: Effect of A-cation size and sintering temperature

In this chapter, the effect of sintering temperature and A-site cation radius on the structural, magnetic and transport properties, a systematic investigation of La$_{0.5}$Nd$_{0.2}$Ca$_{0.3}$–$x$K$_x$MnO$_3$ ($x = 0.0$ and 0.05) nanoparticles has been undertaken. At 700°C,
the XRD peaks show a broad distribution due to nanocrystalline character of samples. Rietveld analysis of X-ray diffraction data confirmed the presence of orthorhombic symmetry with $Pbnm$ space group for all the samples. It can be seen that in both the LCM and LCKM samples, the unit cell volume increases with increase in sintering temperature. Also at same calcinations temperature, the unit cell volume of LCKM samples was found to be higher than those of LCM samples, which is consistent with larger ionic radius of K than Ca. The chemical composition for the constituent elements of the synthesized samples has been analysed by Energy Dispersive X-ray Spectroscopy (EDX). It can be observed from data that the experimental values of mass percentages of all elements (except K) are in good agreement with the theoretical values. The results further confirm that in LCKM samples, vaporization of K occurs during sintering, which becomes more vigorous at 1100°C. The results of iodometric titrations suggest that increase in sintering temperature leads to a decrease in oxygen content of the perovskite ceramics thereby resulting in the formation of oxygen vacancies which become dominant at 1100°C. Scanning electron microscope (SEM) technique was done to investigate the morphology of the samples. To know the morphology and microstructure of nanocrystalline samples, transmission electron microscopy (TEM) measurements of LCM7 and LCKM7 powders calcined at 700°C have been carried out. The average grain sizes of LCM7 and LCKM7 were found to be 30.3 nm and 31.2 nm respectively from TEM. We have examined the effect of sintering temperature as well as size of doped element K on the magnetic as well as transport properties of all the samples. Magnetization measurements have been undertaken as a function of temperature in a zero magnetic field. The results show that all the compounds undergo a transition from paramagnetic to ferromagnetic state with decreasing temperature. It can be seen that the doping of K in LCM samples leads to the increment in $T_c$. The introduction of monovalent K$^+$ for divalent cation Ca$^{2+}$ in LCM leads to increment of the ferromagnetic double exchange (DE) interactions Mn$^{3+}$–O$^{2−}$–Mn$^{4+}$ which are responsible for larger magnetization and higher $T_c$ of K-doped samples. The Curie temperature and magnetization occur to rise sharply with increasing sintering temperature showing the onset of ferromagnetic ordering except for samples at 1100°C. The most probable reason is the increase in oxygen vacancies with sintering temperature, which becomes dominant at 1100°C. The
higher oxygen vacancy in samples sintered at 1100°C therefore leads to a decrease in the number of Mn$^{4+}$ ions and consequently Mn$^{3+}$/Mn$^{4+}$ pairs, which are responsible for ferromagnetism thereby causing smaller magnetization and lower value of $T_c$. The temperature dependence of resistivity $\rho(T)$ of polycrystalline LCM and LCKM samples was measured in zero magnetic field in the temperature range 80-300K. In the high temperature region, $\rho-T$ plot displays a continuous increase in resistivity with decreasing temperature, indicating semiconducting behavior of samples. However, as the temperature drops, the temperature coefficient of resistivity abruptly becomes positive and the phases display metallic nature at a point called metal-semiconductor transition temperatures ($T_{MS}$). These results indicate that the materials are ferromagnetic-metallic at low temperature ($T < T_{MS}$) and become paramagnetic-semiconductor at high temperature ($T > T_{MS}$). It is observed that at same sintering temperature, K-doped samples have lower resistivity and higher $T_{MS}$ than their undoped counterparts which could be explained on the basis of A-site cation radius $<r_A>$. The increase in $<r_A>$ with K doping, because of its larger size, increases the Mn–O–Mn angle. This may result an increase in the tendency of hopping of $e_g$ electrons from Mn$^{3+}$ to Mn$^{4+}$ sites thereby causing a decrease in resistivity and increment in $T_{MS}$. It is observed that resistivity decreases with sintering temperature while there is increase in $T_{MS}$. This could be due to the fact that the grain growth of the samples occurs with rise in sintering temperature which provides a better intergrain connection. However, a reverse trend in resistivity and $T_{MS}$ is observed in samples sintered at 1100°C. This could be due to presence of higher oxygen vacancies in the samples sintered at 1100°C. In the high temperature region, it was observed that the resistivity data was best fitted by SPH model with best agreement factors $R$. 